Shear alignment at two length scales

van Ekenstein, GA; Polushkin, E; Ikkala, O; ten Brinke, G; Ikkala, I.; Nijland, H.

Published in:
Macromolecules

DOI:
10.1021/ma034042u

Publication date:
2003

Shear Alignment at Two Length Scales: Comb-Shaped Supramolecules Self-Organized as Cylinders-*within*-Lamellar Hierarchy

Gert Alberda van Ekenstein,† Evgeny Polushkin,† Harry Nijland,† Olli Ikkala,*,‡ and Gerrit ten Brinke*,†

Laboratory of Polymer Chemistry, Materials Science Centre, Dutch Polymer Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands, and Department of Engineering Physics and Mathematics and Center for New Materials, Helsinki University of Technology, P.O. Box 2200, FIN-02015 HUT, Espoo, Finland

Received January 14, 2003; Revised Manuscript Received March 11, 2003

ABSTRACT: Large-amplitude oscillatory shear alignment of a hierarchically ordered system of comb-shaped supramolecules and the preparation of core−corona nanorods thereof are reported. The supramolecules consist of nearly symmetric polystyrene-*b*-poly(4-vinylpyridine) diblock copolymers with pentadecylphenol side chains hydrogen bonded to the poly(4-vinylpyridine) blocks. The polystyrene blocks, accounting for approximately 20% (w/w) of the supramolecules, are segregated in hexagonally ordered cylinders inside a matrix formed by the comb-shaped poly(4-vinylpyridine)-based blocks. The matrix further self-organizes in a layered structure below the order−disorder transition temperature of 70 °C. Thus, a cylinder-*within*-lamellar morphology is formed. Imposing shear leads to considerable alignment of both structures. The cylinders align along the shear flow with the (10) plane parallel with respect to the shear plane. The matrix layers align perpendicular to the cylinders, transverse to the flow. After elimination of pentadecylphenol by dialysis, crew-cut rods of 20−25 nm in diameter and 5−10 μm in length are obtained.

Introduction

The role of comb-shaped supramolecules as building blocks for functional polymeric materials is by now well-documented.[1−3] Concepts have been introduced to use homopolymer-based comb-shaped supramolecules obtained by attaching side chains (groups) to homopolymers by physical means such as hydrogen bonding or a combination of ionic and hydrogen bonding. Examples of functional properties are directional proton conductivity,[4] electronically conducting nanocylinders,[5] and polarized luminescence.[6] In these cases different aspects of the physically bonded side groups are exploited like doping, self-organization, processability, and cleavability (side chains may be removed in a straightforward way). The homopolymer-based systems self-organize with a characteristic periodicity of ca. 3−5 nm.[7] An additional length scale, very similar to that found in liquid crystalline diblock copolymers,[8] is introduced if such a comb-shaped supramolecule forms one of the blocks of a diblock copolymer. This combination results in self-organized *hierarchically* ordered structures,[1,9] which have been used to create materials with interesting (anisotropic) proton conductivity properties,[1,4] dielectric stacks,[10] functional membranes,[11] and crew-cut nanoobjects.[12] Besides the aspects already mentioned above, the very efficient swelling of the pure diblock copolymer self-organized microphase separated structures by the side groups is an essential new element.

Large-amplitude oscillatory shear is one of the best ways to align and improve the order of the multidomain grain boundary structures obtained by microphase separation of bulk block copolymer systems.[13−19] The effect of shear on the alignment of layered block copolymer systems has been investigated in some detail. Depending on the shear parameters, frequency, temperature, and amplitude, either the parallel or perpendicular orientation is found to be stable.[16−19] The same holds for systems consisting of comb-shaped P4VP(PDP) supramolecules, which are obtained by hydrogen-bonding pentadecylphenol (PDP) molecules to poly(4-vinylpyridine) (P4VP).[20,21] It is well-known that P4VP(PDP)$_{1.0}$ (subscript denotes number of phenol groups per pyridine group) self-organizes in the form of alternating polar and nonpolar layers below the order−disorder transition temperature T_{ODT} of ca. 65 °C.[7,22] Although the glass transition temperature of pure P4VP is at 150 °C, the P4VP(PDP)$_{1.0}$ supramolecules remain in the melt state for temperatures as low as 20 °C where the alkyl side chains start to crystallize.[23]

If P4VP(PDP) is a block of a diblock copolymer-based supramolecule such as PS-*b*-P4VP(PDP), where PS is polystyrene, the above-mentioned additional ordering principle is introduced. This results in characteristic two length scale hierarchically ordered structures such as lamellar-*within*-lamellar or, when the P4VP(PDP) blocks form the minority phase, lamellar-*within*-cylinders and lamellar-*within*-spheres. In the opposite case where the minority phase is formed by PS, a layered P4VP(PDP) matrix is obtained in which hexagonally ordered PS cylinders or bcc ordered PS spheres are present.[1,2,9]

Attempts to align both length scale structures within such hierarchically ordered structures by a shear field poses a problem that can best be illustrated by considering the lamellar-*within*-lamellar ordered system. Here PS and P4VP(PDP) layers alternate and the P4VP(PDP) lamellae consist further of alternating polar and nonpolar layers below the corresponding T_{ODT}. As transmission electron microscopy demonstrates,[1,9] thermodynamics forces the two different lamellar structures to be oriented perpendicular with respect to each other. The problem becomes apparent when a shear field is

† University of Groningen.
‡ Helsinki University of Technology.

10.1021/ma034042u CCC: $25.00
Published on Web 04/15/2003

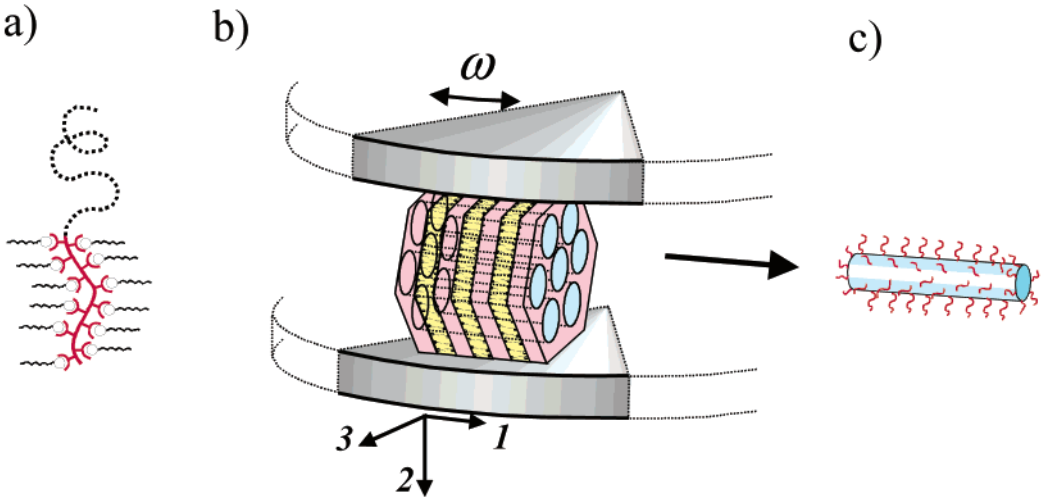

Figure 1. (a) Schematics to construct diblock copolymer/amphiphile supramolecules. (b) The present structural hierarchy with the hexagonally organized PS cylinders within the layered background consisting of P4VP(PDP). The alignment due to large-amplitude oscillatory shear using cone/plate geometry is also indicated. (c) Cleavage of the PDP amphiphiles leads to nanorods containing PS cores and P4VP coronas.

imposed. In the case of the homopolymer-based P4VP(PDP) this external field aligns the alternating polar−nonpolar layers, depending on the shear conditions (frequency, temperature, etc.), parallel or perpendicular to the shear plane.[21] For the layered PS-*b*-P4VP(PDP) above the T_{ODT} of P4VP(PDP), where hierarchical ordering is not present, only parallel orientation was observed.[20] Whether it is possible to fully align both type of layers in the hierarchically ordered system at the same time is still not clear. The results obtained so far seem to indicate that the alternating PS and P4VP(PDP) layers orient parallel and that there is a tendency for the layers inside the P4VP(PDP) layers to orient transverse.[4,24]

In this paper we will consider the situation where the block lengths of PS-*b*-P4VP are selected in such a way that after hydrogen bonding P4VP with PDP a hexagonally ordered structure of PS cylinders in a P4VP(PDP) matrix is obtained. The P4VP(PDP) matrix in turn orders below ca. 70 °C in a layered structure. We will demonstrate that in this case a very good alignment of both structures can be obtained by imposing shear. This material will subsequently form the basis for the straightforward production of long nanorods consisting of a PS core and a corona of relatively short P4VP blocks.

Experimental Section

Sample Preparation. Polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP, obtained from Polymer Source Inc.) has a M_w = 21 400 and 20 700 g/mol for the PS and P4VP block, respectively. The polydispersity of the block copolymer is M_w/M_n = 1.13. To obtain the comb-shaped PS-*b*-P4VP(PDP) supramolecule, PS-*b*-P4VP is hydrogen bonded with a stoichiometric (with respect to the number of pyridine groups) amount of 3-*n*-pentadecylphenol (PDP). PDP (Aldrich) was recrystallized twice from petroleum ether (40−60 w/w) and dried in a vacuum at 40 °C. The samples were prepared by mixing PS-*b*-P4VP and PDP in analysis grade chloroform, keeping the concentration below 2 wt % to ensure homogeneous complex formation. After stirring for 2 h, the solvent was allowed to evaporate very slowly, and the sample was further dried in a vacuum at 50 °C.

To prepare crew-cut nanorods, after the alignment procedure a part of the sample was placed in a dialysis tube of 29 mm diameter (SERVAPOR, cutoff M = 12 000, Serva) filled with ethanol and dialyzed against ethanol as described previously.[12]

Rheology. Shearing was carried out with a AR 1000N rheometer (TA Instruments) in oscillatory mode with a cone−plate geometry (4° cone, 20 mm diameter). The oscillatory shear was performed with constant shear frequency of 1 Hz and strain amplitude of 50%. The sample was first sheared for 1 h at 130 °C and then sheared during cooling at 2 °C/min to 50 °C.

Thermal Analysis. Temperature-modulated scanning calorimetry was performed using a DSC 2920 (TA Instruments). All measurements used a heating rate of 1 °C/min, an oscillation amplitude of 1 °C, and an oscillation period of 60 s.

Scanning Transmission Electron Microscopy. STEM was performed with a JEOL 6320 field emission scanning electron microscope equipped with a transmission detector. A drop of the dilute crew-cut rod suspension was placed onto a gold grid with a carbon layer. Samples were examined without staining.

Small-Angle X-ray Scattering. SAXS measurements were carried out at room temperature using a NanoStar camera (Bruker and Anton Paar). A ceramic fine-focus X-ray tube, powered with a Kristallflex K760 generator at 35 kV and 40 mA, has been used in point focus mode. The primary X-ray flux is collimated using cross-coupled Göbel mirrors and a pinhole of 0.1 mm in diameter providing a Cu Kα radiation beam with a full width at half-maximum of about 0.2 mm at the sample position. The sample−detector distance was 1.04 m. The scattering intensity was registered by a Hi-Star position-sensitive area detector (Siemens AXS) in the q range of 0.1−2.0 nm^{-1}. The scattering vector q is defined as $q = (4\pi/\lambda)\sin(\theta/2)$, where λ = 0.1542 nm and θ is the scattering angle. The measuring time was 30 min.

Results and Discussion

The comb-shaped PS-*b*-P4VP(PDP) supramolecules considered here, obtained by hydrogen-bonding pentadecylphenol (PDP) molecules to the poly(4-vinylpyridine) (P4VP) block of a nearly symmetric diblock copolymer with polystyrene (PS), self-organize in the form of hexagonally ordered PS cylinders in the P4VP(PDP) matrix (see Figure 1b), as will be shown further on by SAXS (Figure 3). This is the expected morphology since the presence of one PDP molecule per pyridine unit implies a weight fraction of the PS phase of approximately 20%. SAXS demonstrates that this cylindrical morphology is

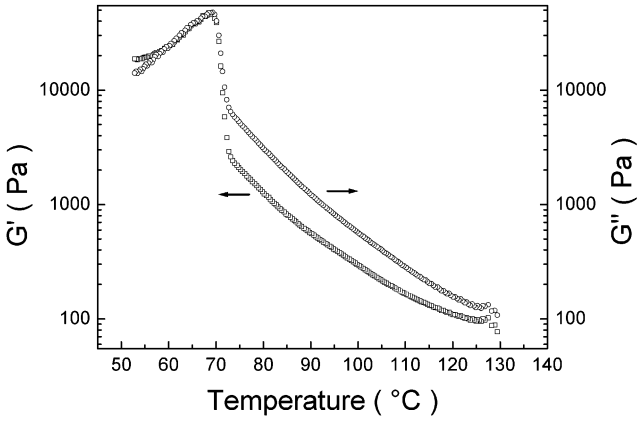

Figure 2. Shear moduli of PS-*b*-P4VP(PDP) as a function of temperature during oscillatory shearing (1 Hz, 50% strain amplitude) and cooling from 130 to 50 °C at 2 °C/min.

present up to elevated temperatures; an order−disorder transition has not been observed. The matrix consisting of the comb-shaped supramolecule blocks (see Figure 1b), on the other hand, exhibits a transition from the lamellar to the disordered state at the order−disorder transition temperature T_{ODT} of approximately 70 °C.[7,24] Below that temperature we are dealing with a *hierarchically* structured material with two characteristic length scales that are about an order of magnitude different, 30 and 3.9 nm.

To induce macroscopic alignment, we applied large-amplitude oscillatory shear first during 1 h at 130 °C and then during cooling with 2 °C/min. Differential scanning calorimetry (DSC) data, to be discussed further on, provide no clear evidence for the vitrification of the PS cylinders, but as will be shown, the presence of a glass transition in the vicinity of the short length scale T_{ODT} of 70 °C cannot be excluded. As for the matrix, on cooling it remains in the fluid state down to temperatures as low as room temperature where the alkyl chains crystallize.[23] Thus, the shearing procedure could be easily continued on passing through the T_{ODT} of 70 °C down to 50 °C. Figure 2 shows the shearing moduli as a function of temperature during this cooling procedure. We observe gradually increasing values for the elastic and the loss modulus until ca. 70 °C, where a sudden sharp upturn signals the order−disorder transition to a lamellar morphology of the P4VP(PDP) matrix.

The sheared sample was examined by ex-situ SAXS measurements performed with the sample in the three different orientations: normal, radial, and tangential with respect to the cone−plate geometry used. The tangential view, i.e., obtained with the incident X-ray beam along the shear direction, is presented in Figure 3a. It demonstrates that the PS cylinders are very well ordered along the flow in a hexagonal lattice. The first-order scattering peaks are observed at $q^* = 0.21$ nm^{-1}, corresponding to a distance of 34 nm between the PS cylinders. Furthermore, the picture shows that the PS cylinders are preferentially aligned in such a way that the (10) plane is parallel to the shear plane (Figure 3b). Although alignment with the (10) plane perpendicular to the shear flow plane has been observed for hexagonally ordered systems, this is, as in the case of a lamellar morphology, believed to be stable only at temperatures close to the corresponding order−disorder temperature.[19] As mentioned before, the highest temperature of 130 °C used in our case is far below a

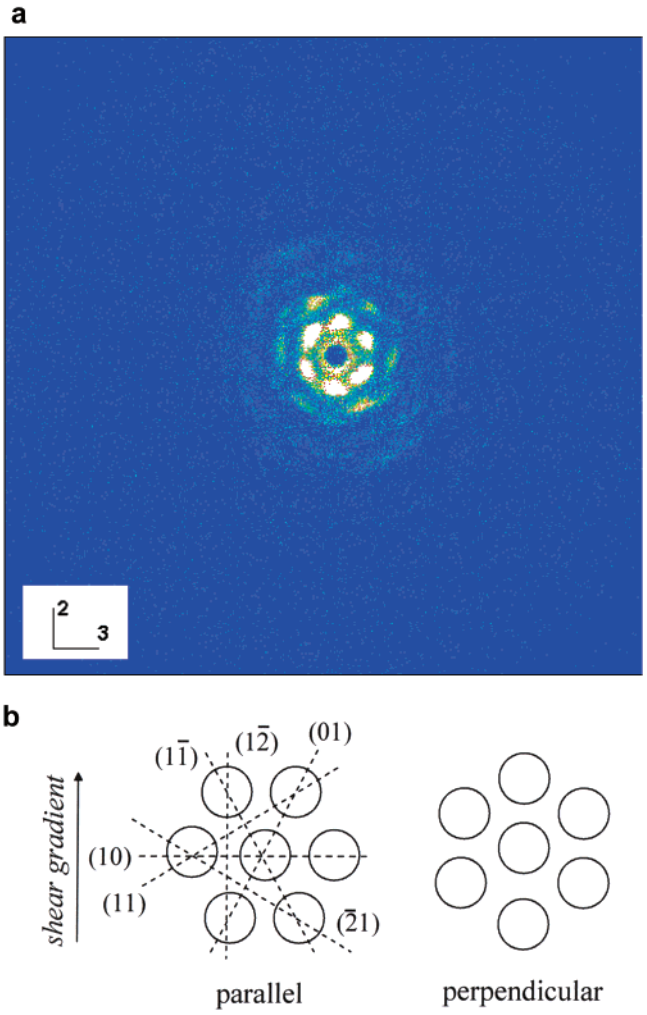

Figure 3. (a) SAXS of shear aligned PS-*b*-P4VP(PDP): tangential view. (b) Cartoon of cylinders aligned along shear direction. Parallel: (10) plane parallel to shear plane. Dashed lines indicate crystallographic planes in the hexagonal lattice. Perpendicular: (10) plane perpendicular to shear plane.

possible order−disorder transition of the hexagonal structure. Another interesting feature of the tangential pattern shown in Figure 3a is the absence of any scattering from the layered matrix structure, which, if observed, would be visible at larger angles near the edge of the figure. The radial and normal scattering patterns are presented in Figure 4a,b. Strong point like meridional reflections at $q^* = 0.21$ nm^{-1} and at $\sqrt{3}q^*$ confirm the very good alignment of the PS cylinders along the flow direction. The presence of both reflections indicates that there is a significant angular distribution of the PS cylinders orientation around the preferred parallel orientation (Figure 3b). The radial pattern shows a very strong q^* reflection from the (10) planes and very weak $\sqrt{3}q^*$ reflection from the (11) and ($\bar{2}$1) planes (see Figure 3b). Compared with the radial pattern, the normal pattern shows a much stronger $\sqrt{3}q^*$ reflection from the (1$\bar{2}$) planes and much weaker reflection from the (01) and (1$\bar{1}$) planes. This is in good agreement with the preferred parallel orientation. The high-intensity equatorial reflections at large angles, $q_s^* = 1.59$ nm^{-1}, in Figure 4a,b correspond to the layered structure of the P4VP(PDP) matrix. The presence of these reflections here together with their absence in Figure 3a demonstrates that these layers have a transverse orientation

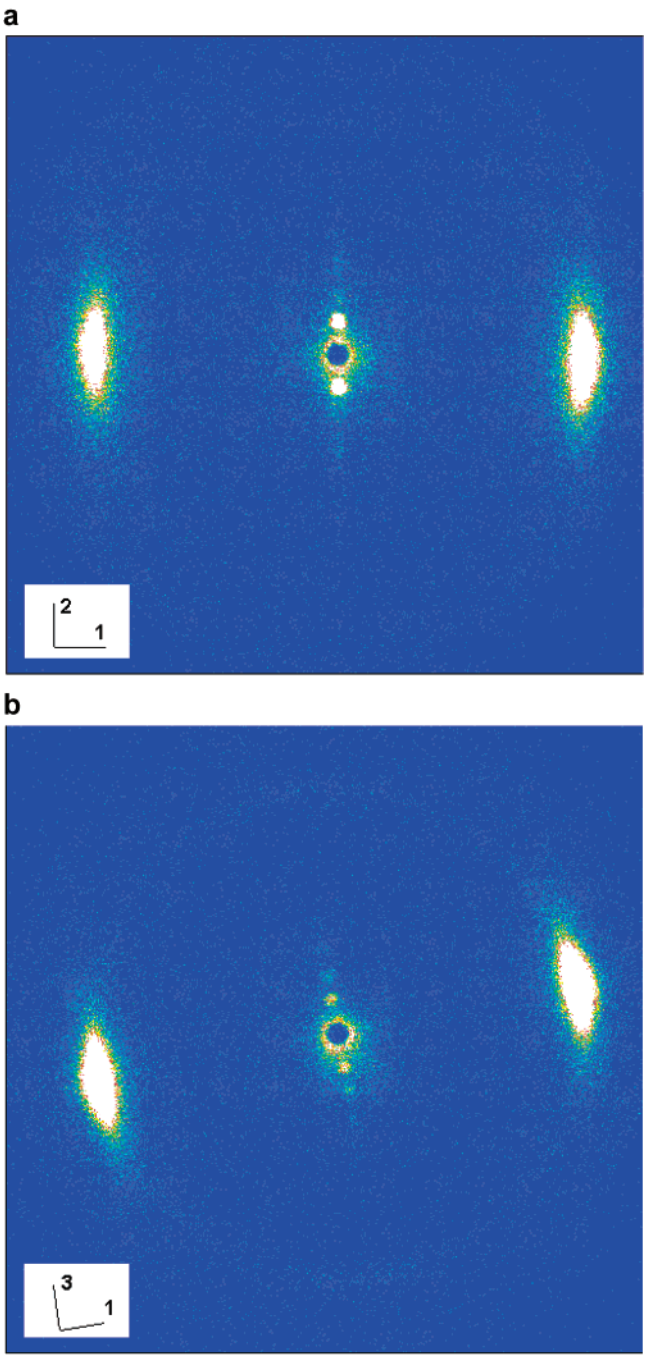

Figure 4. SAXS of shear-aligned PS-*b*-P4VP(PDP): (a) radial view; (b) normal view.

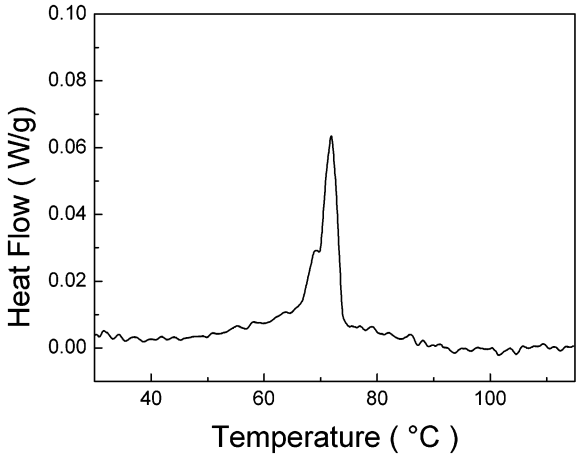

Figure 5. Modulated DSC curves on heating of PS(20.7K)-*b*-P4VP(21.4K)-based systems: total heat flow of shear-aligned PS-*b*-P4VP(PDP).

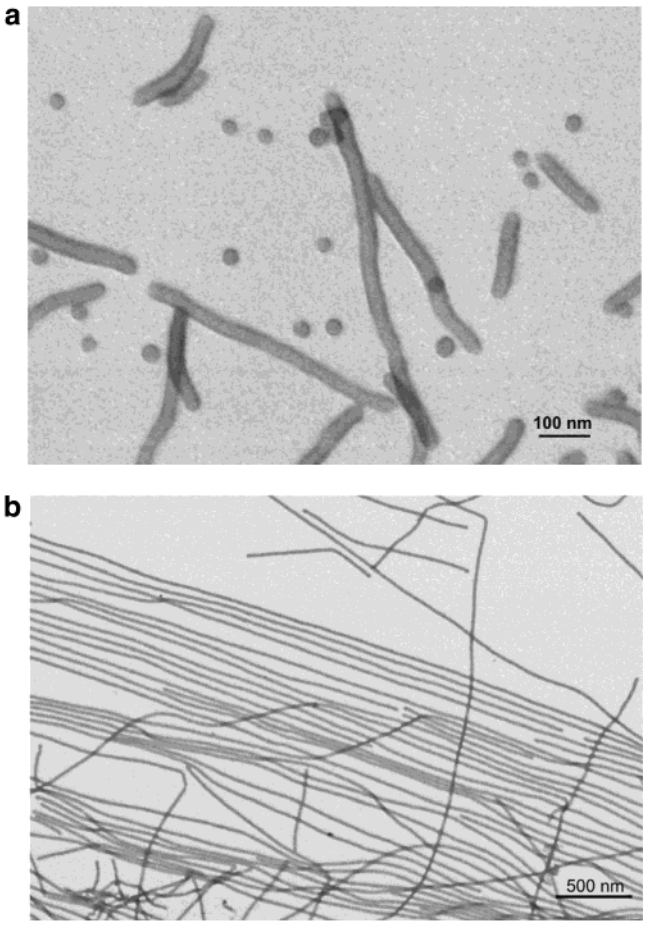

Figure 6. STEM pictures of cylindrical nanorods of PS(20.7K)-*b*-P4VP(21.4K) diblock copolymers: (a) before shear alignment; (b) after shear alignment.

with respect to the shear flow. In conventional diblock copolymers, transverse alignment of layers has never been observed to be stable. In our case the overriding factor for the stable transverse orientation seems to be of thermodynamic origin. Thermodynamics apparently forces the two length scale structures to be perpendicular with respect to each other, since this mutual orientation is invariably observed by transmission electron microscopy studies of nonsheared samples.[1,9]

Summarizing the SAXS data, we see that the hexagonally ordered PS cylinders align with the (10) plane parallel to the shear plane inside the P4VP(PDP) matrix which further self-organizes into layers aligned transversely with respect to the flow. There is another interesting example of shear orientation of a somewhat similar hierarchically ordered system. Thomas and coworkers[8] studied the oscillatory shear orientation of a PS-*b*-PILC block copolymer consisting of a polystyrene block and a liquid crystalline side chain polyisoprene (PI)-based block. As in our case, a hierarchically ordered material is obtained with PS cylinders inside a smectic LC mesophase (below 165 °C). As in our case, the normal of the smectic layers is parallel to the cylinder axis. Shearing of the smectic LC mesophase, however, led to a transverse orientation of the PS cylinders and a perpendicular orientation of the smectic layers. Ap-

parently, the mesogenic character of the side chain, compared to our flexible PDP side chains, is responsible for this difference in shear-induced orientation.

Figure 5 presents the total heat flow of the shear-aligned sample obtained by modulated DSC with an underlying heating rate of 1 °C/min and further modulated with a sinusoidal signal of 1 °C amplitude and period of 60 s. The order−disorder transition of the P4VP(PDP) blocks is clearly present as an endothermic peak with a low-temperature shoulder. This shoulder might well be due to less well-ordered domains having a lower order−disorder transition temperature in analogy with melting in semicrystalline polymers. There is no sign of a glass transition T_g of the PS cylinders or, of course, of the P4VP(PDP) matrix, which is to be expected since P4VP(PDP) is well-known to remain in the melt state to temperatures as low as 20 °C where the alkyl layers crystallize.[23] At this point we cannot exclude that the T_g of the PS cylinders is hidden under the endothermic ODT peak, although the reversible heat flow measurement also provides no clear evidence of a T_g of the PS cylinders.

In the Introduction we already mentioned that PDP-like amphiphiles are very efficient swelling agents. In the case considered here, hexagonally ordered PS cylinders are obtained from PS-*b*-P4VP diblock copolymers of similar block lengths. Realizing that, apart from the block lengths, the fraction of amphiphiles may be varied as well, even considerably exceeding the stoichiometric amount, it becomes clear that these kind of supramolecules are ideally suited to prepare core−corona nanorods (see Figure 1c). The relative thickness of the corona with respect to the core can be tailored, including crew-cut-type structures with a very thin corona. To investigate the effect of shear alignment on the nanorod properties, in particular their length, the shear-aligned sample was used. Nanorods of a PS core and P4VP corona were prepared by removing the hydrogen-bonded PDP molecules by the dialysis procedure described in the Experimental Section.

To compare nanorods obtained from an unaligned sample[12] with those obtained from the shear-aligned sample, Figure 6 presents the two corresponding scanning transmission electron microscopy pictures. The effect of the large-amplitude oscillatory shear procedure is very clear: after shear the rods are an order of magnitude longer (several micrometers), and the micellar structures, shown in Figure 6a, are not present anymore.

Summary

Oscillatory shear orientation of hierarchically ordered PS-*b*-P4VP(PDP) systems of a cylinder-*within*-lamellar morphology results in parallel alignment of the PS cylinders with the *(10) plane parallel to the shear plane* and *transverse* alignment of the matrix layers. Using the shear flow procedure, PS-*b*-P4VP nanorods of up to 10 μm length can easily be prepared.

Acknowledgment. Dr. Andrei Subbotin is acknowledged for useful discussions.

References and Notes

(1) Ruokolainen, J.; Mäkinen, R.; Torkkeli, M.; Mäkelä, T.; Serimaa, R.; ten Brinke, G.; Ikkala, O. *Science* **1998**, *280*, 557.
(2) Ikkala, O.; ten Brinke, G. *Science* **2002**, *295*, 2407.
(3) Ikkala, O.; ten Brinke, G. In *Handbook of Advanced Electronic and Photonic Materials and Devices*; Nalwa, H. S., Ed.; Academic Press: New York, 2000; Vol. 8, Chapter 5, pp 185−208.
(4) Mäki-Ontto, R.; de Moel, K.; Polushkin, E.; Alberda van Ekenstein, G.; ten Brinke, G.; Ikkala, O. *Adv. Mater.* **2002**, *14*, 357.
(5) Koskonen, H.; Ruokolainen, J.; Knaapila, M.; Torkkeli, M.; Serimaa, R.; ten Brinke, G.; Bras, W.; Monkman, A.; Ikkala, O. *Macromolecules* **2000**, *33*, 8671.
(6) Knaapila, M.; Ikkala, O.; Torkkeli, M.; Jokela, K.; Serimaa, R.; Dolbnya, I. P.; Bras, W.; ten Brinke, G.; Horsburgh, L. E.; Palson L.-O.; Monkman, A. P.; Ikkala, O. *Appl. Phys. Lett.* **2002**, *81*, 1489.
(7) Ruokolainen, J.; Torkkeli, M.; Serimaa, R.; Komanschek, B. E.; Ikkala, O.; ten Brinke, G. *Phys. Rev. E* **1996**, *54*, 6646.
(8) Osuji, C.; Zhang, Y.; Mao, G.; Ober, C. K.; Thomas, E. L. *Macromolecules* **1999**, *32*, 7703.
(9) Ruokolainen, J.; ten Brinke, G.; Ikkala, O. *Adv. Mater.* **1999**, *11*, 777.
(10) Kosonen, H.; Valkama, S.; Ruokolainen, J.; Torkkeli, M.; Serimaa, R.; ten Brinke, G.; Ikkala, O. *Eur. Phys. J. E* **2003**, *10*, 69.
(11) Mäki-Ontto, R.; de Moel, K.; de Odorico, W.; Ruokolainen, J.; Stamm, M.; ten Brinke, G.; Ikkala, O. *Adv. Mater.* **2001**, *13*, 107.
(12) De Moel, K.; Alberda van Ekenstein, G. O. R.; Nijland, H.; Polushkin, E.; ten Brinke, G.; Mäki-Ontto, R.; Ikkala, O. *Chem. Mater.* **2001**, *13*, 4580.
(13) Keller, A.; Pedemonte, E.; Willmouth, F. M. *Nature (London)* **1970**, *225*, 538; *Kolloid Z. Z. Polym.* **1970**, *238*, 2329.
(14) Hadziioannou, G.; Mathis, A.; Skoulios, A. *Colloid Polym. Sci.* **1979**, *257*, 136. Hadziioannou, G.; Picot, C.; Skoulios, A.; Ionescu, M.-L.; Mathis, A.; Duplessix, R.; Gallot, Y.; Lingelser, J.-P. *Macromolecules* **1982**, *15*, 263.
(15) Koppi, K.; Tirrell, M.; Bates, F. S.; Almdal, K.; Colby, R. H. *J. Phys. II* **1992**, *2*, 1941.
(16) Fredrickson, G. H.; Bates, F. S. *Annu. Rev. Mater. Sci.* **1996**, *26*, 501.
(17) Chen, Z.-R.; Kornfield, J. A.; Smith, S. D.; Grothaus, J. T.; Satkowski, M. M. *Science* **1997**, *277*, 1248.
(18) Zhang, Y.; Wiesner, U. *Macromol. Chem. Phys.* **1998**, *199*, 1771.
(19) Tepe, T.; Schultz, M. F.; Zhao, J.; Tirrell, M.; Bates, F. S. *Macromolecules* **1995**, *28*, 3008.
(20) Mäkinen, R.; Ruokolainen, J.; Ikkala, O.; De Moel, K.; ten Brinke, G.; De Odorico, W.; Stamm, M. *Macromolecules* **2000**, *33*, 3441.
(21) De Moel, K.; Mäkinen, R.; Stamm, M.; Ikkala, O.; ten Brinke, G. *Macromolecules* **2001**, *34*, 2892.
(22) Ruokolainen, J.; Torkkeli, M.; Serimaa, R.; Komanschek, B. E.; ten Brinke, G.; Ikkala, O. *Macromolecules* **1997**, *30*, 2002.
(23) Luyten, M. C.; Alberda van Ekenstein, G. O. R.; ten Brinke, G.; Ruokolainen, J.; Ikkala, O.; Torkkeli, M.; Serimaa, R. *Macromolecules* **1999**, *32*, 4404.
(24) Polushkin, E.; Alberda van Ekenstein, G. O. R.; Dolbnya, I. P.; Bras, W.; Ikkala, O.; ten Brinke, G. *Macromolecules* **2003**, *36*, 1421.

MA034042U